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A Temperature-Resolved Synchrotron X-ray Diffraction Study of Thermal Decomposition in Cation-Exchanged Hydrotalcite

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Introduction: In the family of hydrotalcite minerals, trivalent cations within brucite-like octahedral sheets generate a net positive charge that is electrostatically balanced by anionic groups in the interlayer. It has long been known that these so-called anionic clays will readily exchange their interlayer species, but recently Komarneni et al. (1998) made the surprising observation that these clays also can remove significant quantities of dissolved transition metal *cations* in solution, such as Co^{2+} , Ni^{2+} , Zn^{2+} , and Cu^{2+} , at room temperature. Based on their measurements of changes in fluid chemistry, these authors argued for a direct exchange between the transition metals in solution and the structural Mg cations that compose the octahedral sheets. Our investigation was intended to confirm the proposed exchange model and to determine the thermal stability of exchanged hydrotalcite-like clays.

Methods and Materials: Commercially prepared 3R hydrotalcite powders (0.05 gm) with composition $\{[\text{Mg}_6^{2+}\text{Al}_2^{3+}(\text{OH})_{16}]^{2+} \cdot [\text{CO}_3 \cdot 4\text{H}_2\text{O}]^{2-}\}$ were equilibrated at room temperature in 25 ml solutions containing 0.01 M of CuCl_2 and, separately, ZnCl_2 for 24 hr at room temperature at pH 4-5. Synchrotron X-ray diffraction data for the dried powders were collected at Beamline X7B, National Synchrotron Light Source, Brookhaven National Labs using a Mar345 imaging plate. End-member and exchanged hydrotalcite phases were continuously heated from 25°C to 415°C in 120 minutes, and 60 s exposures were obtained every 7.5°C.

Results: Our Rietveld analyses of metal-exchanged hydrotalcite-like clays using synchrotron X-ray powder diffraction support the proposed exchange model. Rietveld analyses of the starting and reacted powders were well-behaved with final weighted residuals below 4.0. Occupancy factors for the octahedral sites in the cuprous hydrotalcite refined to 31% Cu and 69% Mg, and the octahedral occupancy factors for Zn-exchanged hydrotalcite were 21% Zn and 79% Mg. On heating, the *c*-axis of the rhombohedral cell remained virtually constant (23.0 Å) until ~170°C, at which point *c* abruptly decreased to 19.8 Å.

Conclusions: We interpret the structural collapse of hydrotalcite at 170°C as resulting from the loss of water molecules from the interlayer with the retention of carbonate groups. This model is consistent with thermogravimetric data presented in Bellotto et al. (1996), who revealed a major water loss episode in hydrotalcite over the interval 150 °C to 200 °C. At ~300°C, this intermediate hydrotalcite-like phase decomposed entirely to periclase, coincident with the onset of decarbonation at 300 °C observed by Bellotto et al. (1996). In contrast, cuprous hydrotalcite exhibited no evidence for an intermediate collapsed structure before its complete decomposition at ~300°C.

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